Proposed Field Sampling and Sample Preparation Changes for Soils Containing Metallic Residues

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Project Team

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- Larry Penfold: Test America
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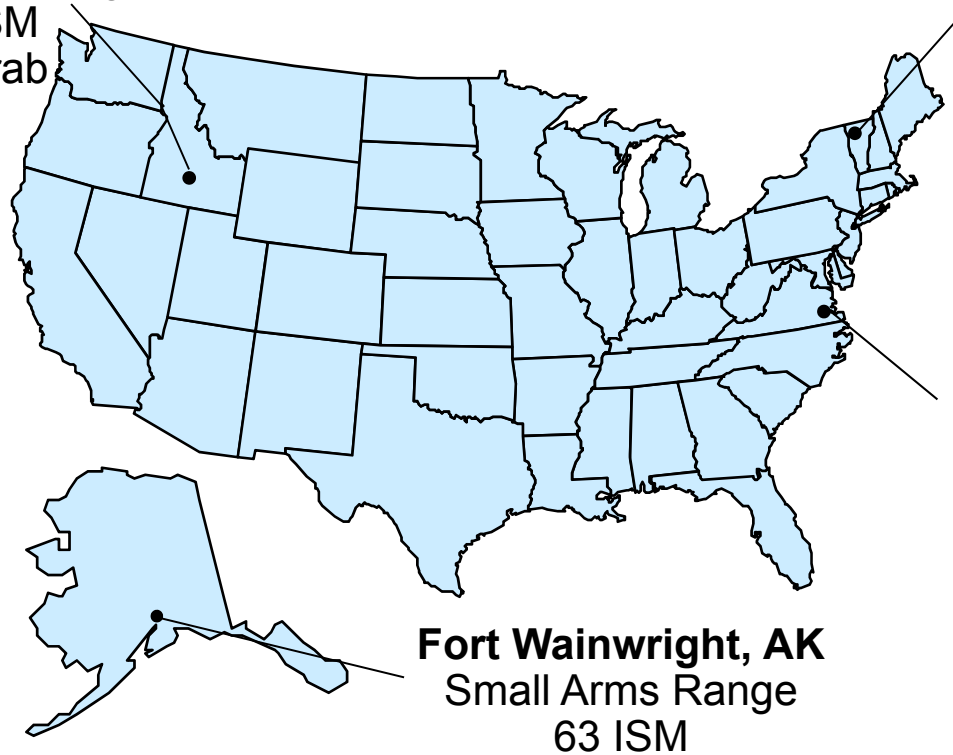
Study Objectives

- Demonstrate improved data quality for metal constituents in surface soils on military training ranges by coupling multi-increment sampling with modifications to sample preparation and analysis methods such as:
  - ♦ Field sampling
  - ♦ Sample processing involving grinding
  - ♦ Sub-sampling to build the digestate aliquot
  - ♦ Larger digestion mass
  - ♦ Laboratory processing protocol applicable to both metals and energetics

Demonstration Sites



Kimama, ID
Small Arms Range
21 ISM
30 Grab

Camp Ethan Allen, VT
Small Arms Range
43 ISM
36 Grab

Fort Eustis, VA
Small Arms Range
27 ISM
33 Grab

Fort Wainwright, AK
Small Arms Range
63 ISM
52 Grab

Performance Assessment

- ISM versus Grab samples
- Number of increments/decision unit
- Field splitting appropriateness
- Grinding necessity
- Grinder comparisons
- Milling Sample Contamination
- Puck Mill and Roller Mill optimum grinding interval
- Digestion mass evaluation
- Digestion time
- Digestion reagent mixture
- **Digestion subsampling preparation**
- **Blank material selection**

ISM versus Grab Samples

Grid Discrete/Grab

951	868	1061	2868	217	2623	1767	1213	692	44
938	2307	319	19,038	1060	1952	3537	9235	5328	79,020
127	352	1204	1977	809	986	2840	4858	2349	1848

Lead (mg/kg)

	<1,000
	1000-10,000
	>10,000

Biased Random Discrete/Grab

555					1930			1851	
		479							
		501					1650		

	ISM (200-inc)	Grab	Grab
	Systematic Random	Grid	Biased Random
n	30	30	6
Mean	2,717	5,060	1,161
Median	2,718	1,238	1,103
Min	2,440	44	479
Max	2,936	79,020	1,930
STD	119	14,438	718
RSD	4	285	62

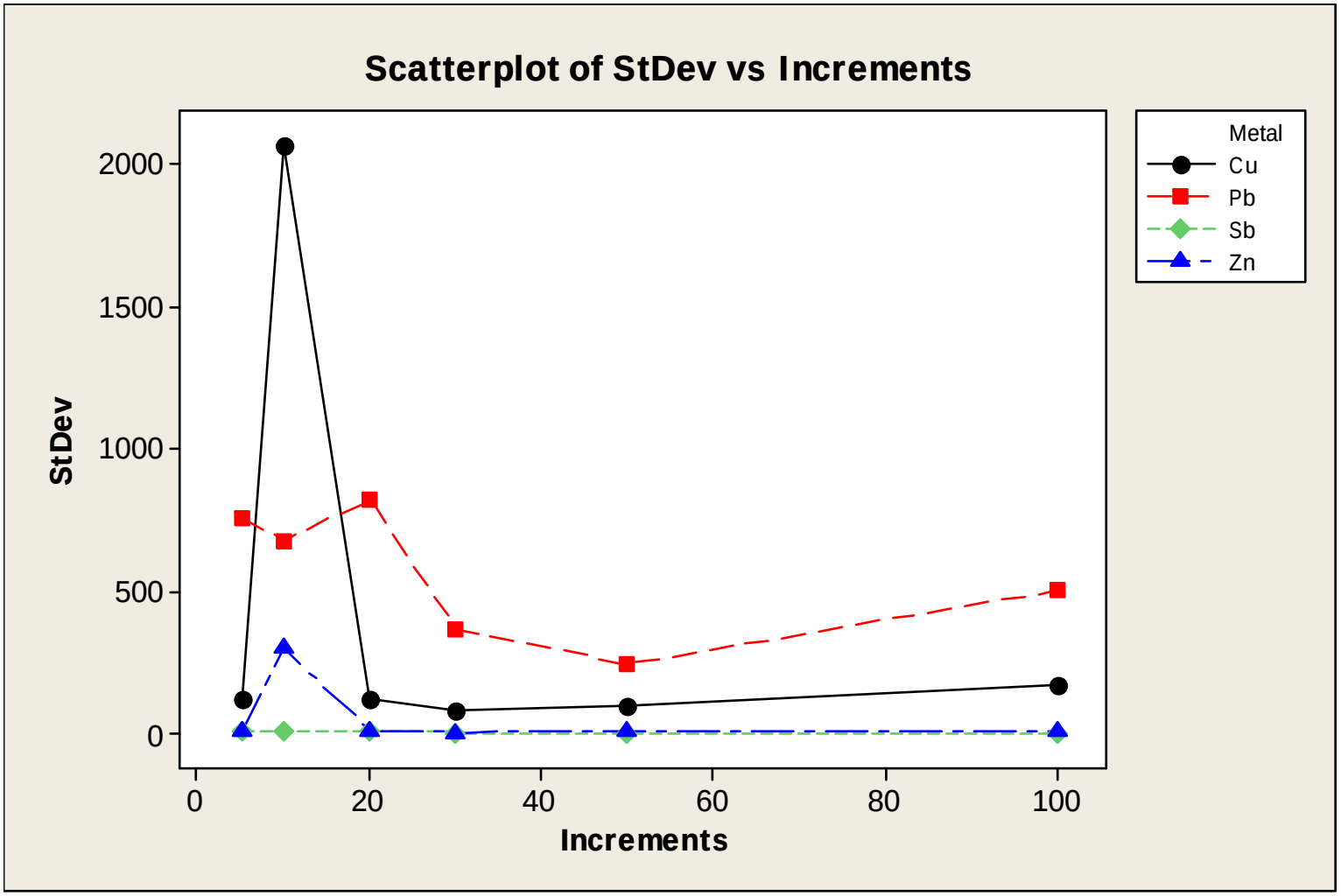
Probability of finding 1 hotspot with six grab samples is 44%. Finding both is 8%

Number of Increments

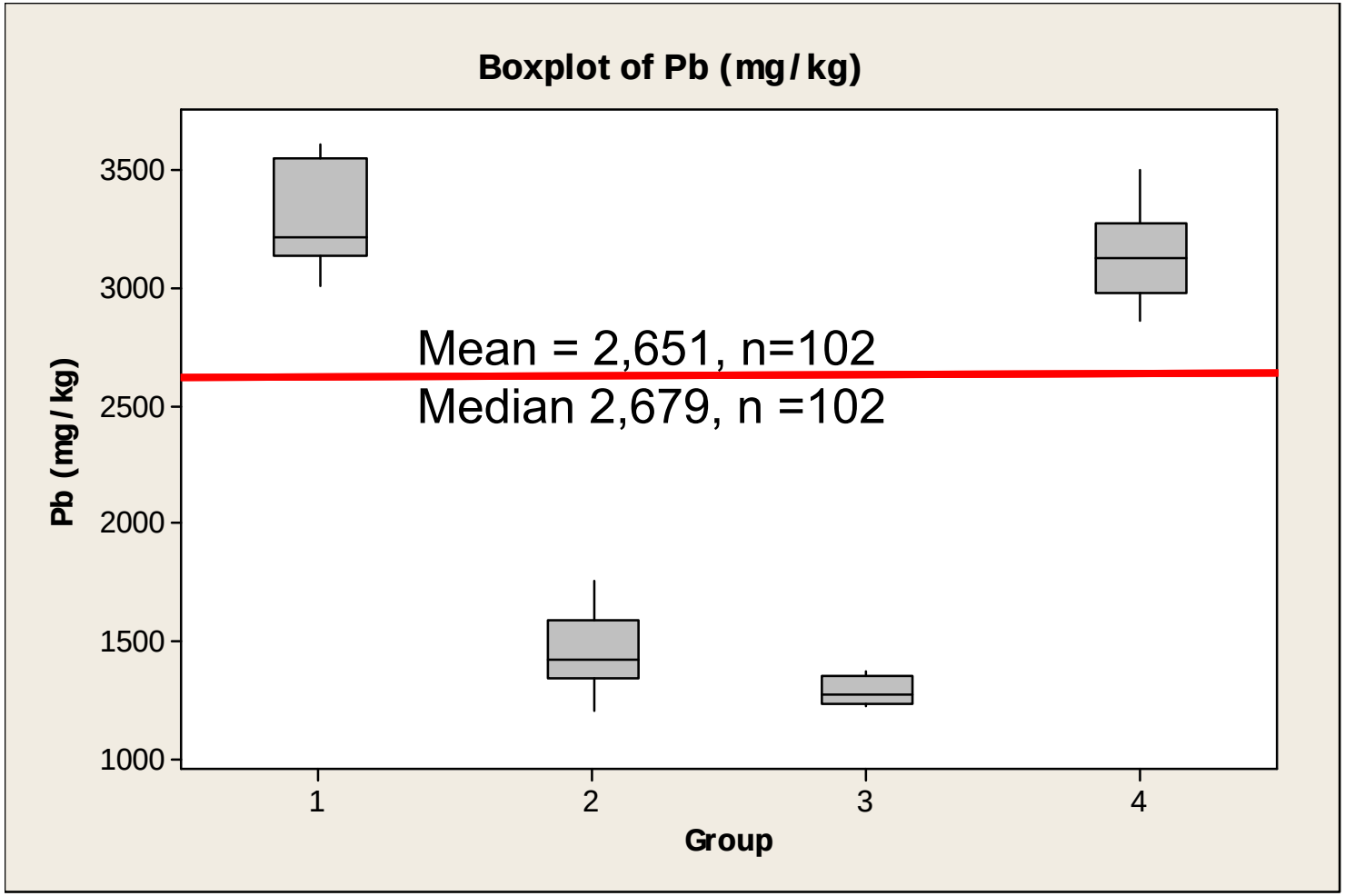
ISM	Percent Relative Standard Deviation (RSD)									
n	Al	Cr	Cu	Fe	Mn	Ni	Pb	Sb	V	Zn
5	3	10	22	4	4	3	25	25	6	9
10	8	6	162	4	4	4	32	63	5	154
20	27	121	26	22	18	26	30	50	32	15
30	3	7	15	10	4	3	14	15	6	6
50	3	15	21	10	2	4	11	11	6	10
100	3	7	26	4	2	2	17	17	3	15
200	6	3	18	4	5	2	4	7	1	11
n = number of increments per MI sample										

Performance criteria RSD < 15% for lab replicates (for concentrations > 100 mg/kg)

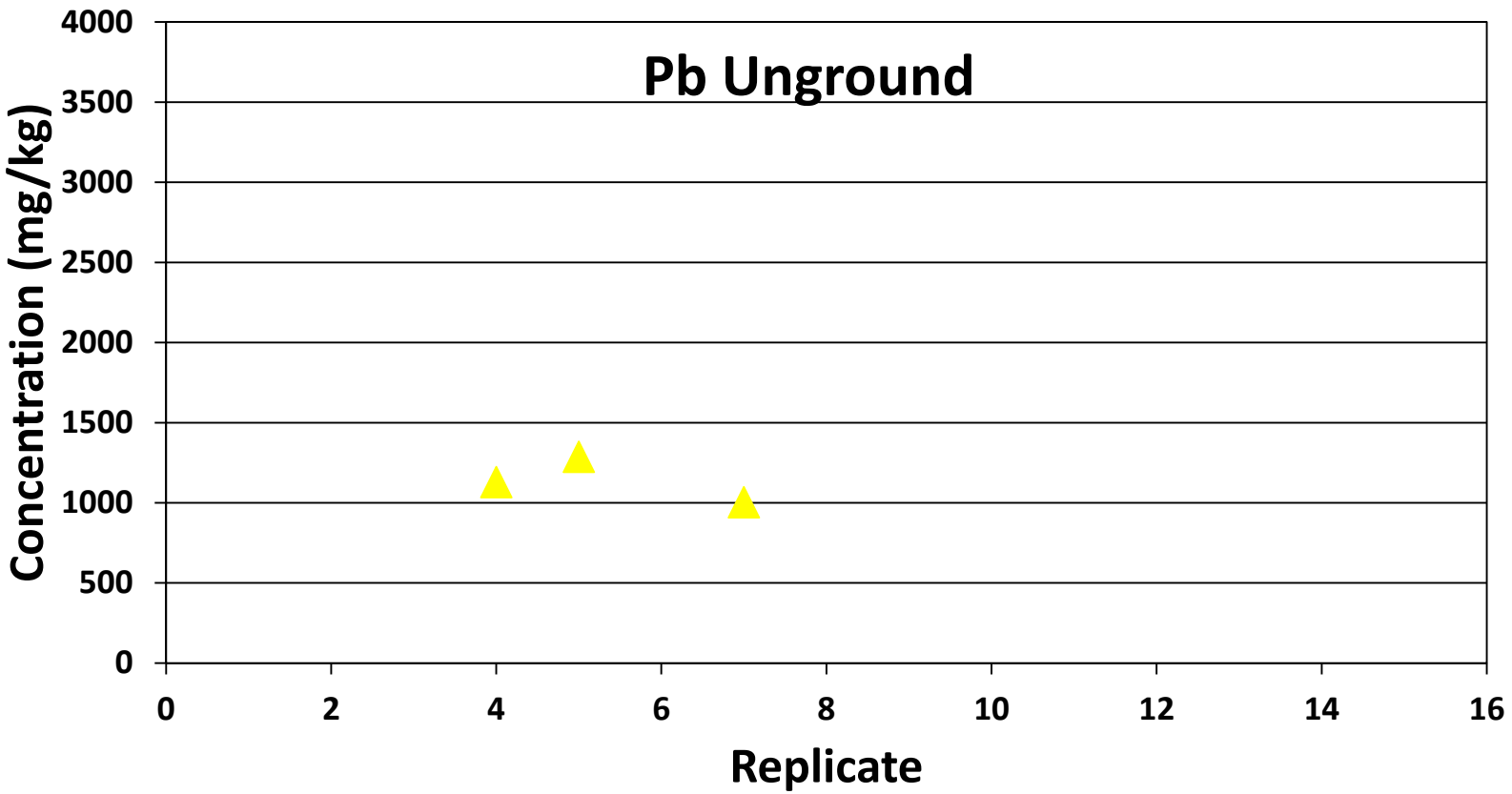
Number of Increments



Field Splitting Appropriateness



To Grind or Not To Grind



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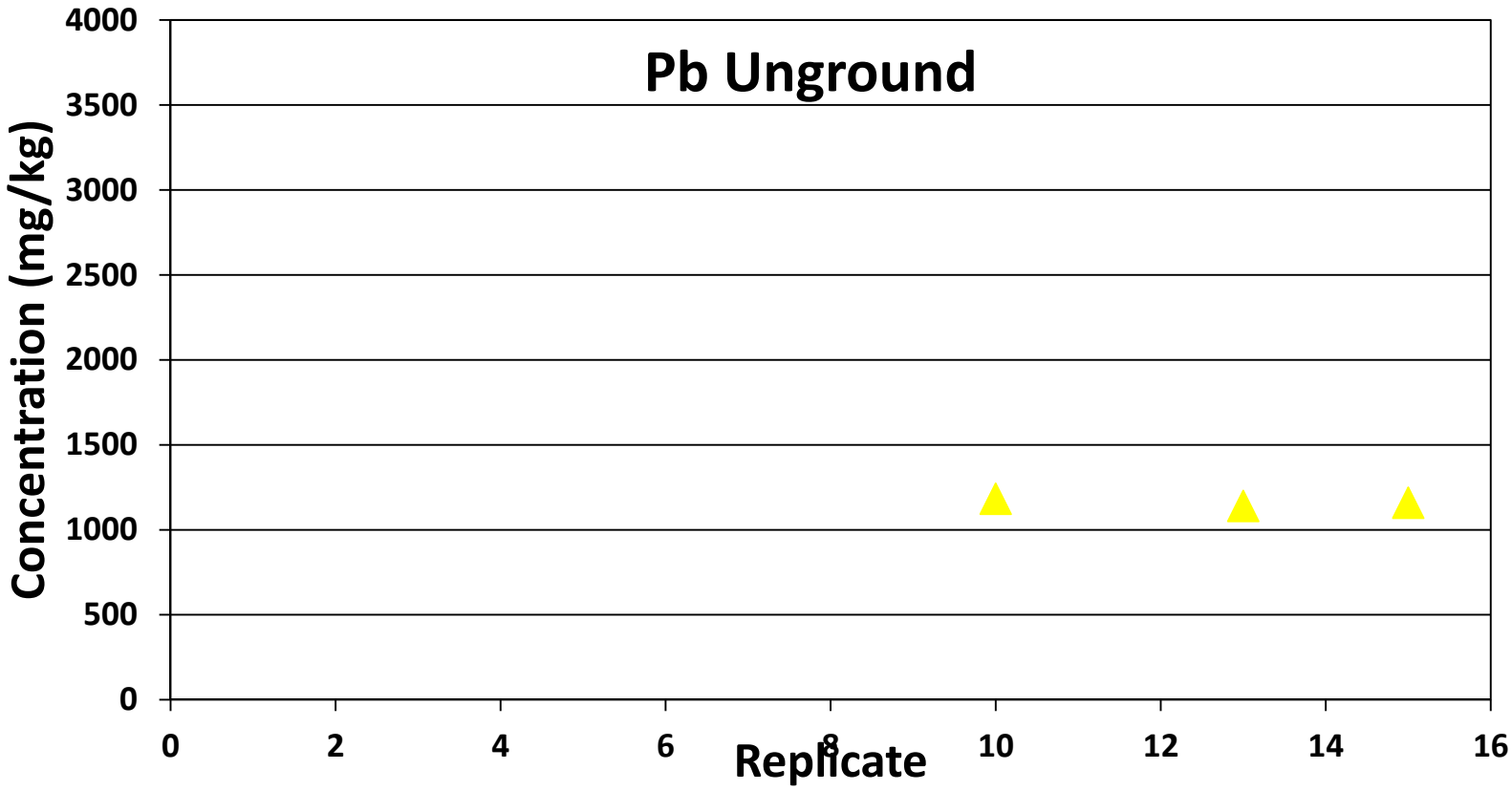

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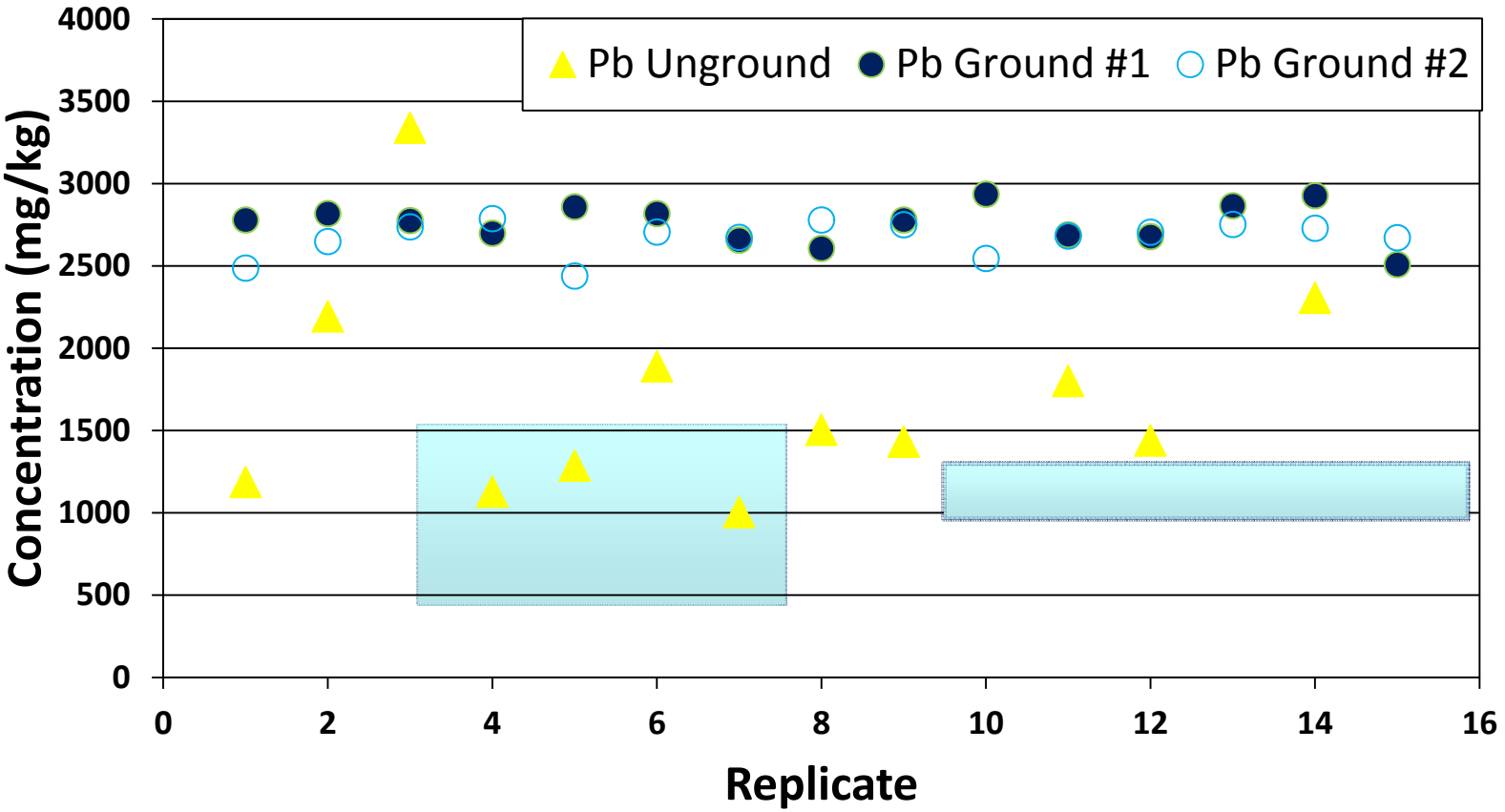


Milling Equipment Comparisons

	Percent Relative Standard Deviation (RSD)									
Machine Type	Al	Cr	Cu	Fe	Mn	Ni	Pb	Sb	V	Zn
Unground #1	4	5	**257**	4	4	7	**61**	**116**	4	**162**
Unground #2	2	5	**25**	1	1	2	**39**	**69**	NA	**17**
Mortar & Pestle	5	4	**39**	4	3	3	**32**	**55**	4	**28**
Puck Mill #1	5	4	10	4	4	4	15	**21**	5	5
Puck Mill #2	1	2	15	4	2	1	4	7	2	10
Puck Mill #3	5	1	**16**	3	2	2	4	5	2	11
Puck & Ring Mill	6	5	5	4	5	5	5	8	5	6
Ball Mill	1	1	3	1	1	1	1	8	1	2
NA-not analyzed, Bolded values > 15%										

Performance Assessment – Sample Processing (Grinding) of Soil

Puck Mill

Fe, Mn, Cr, V

Roller Mill

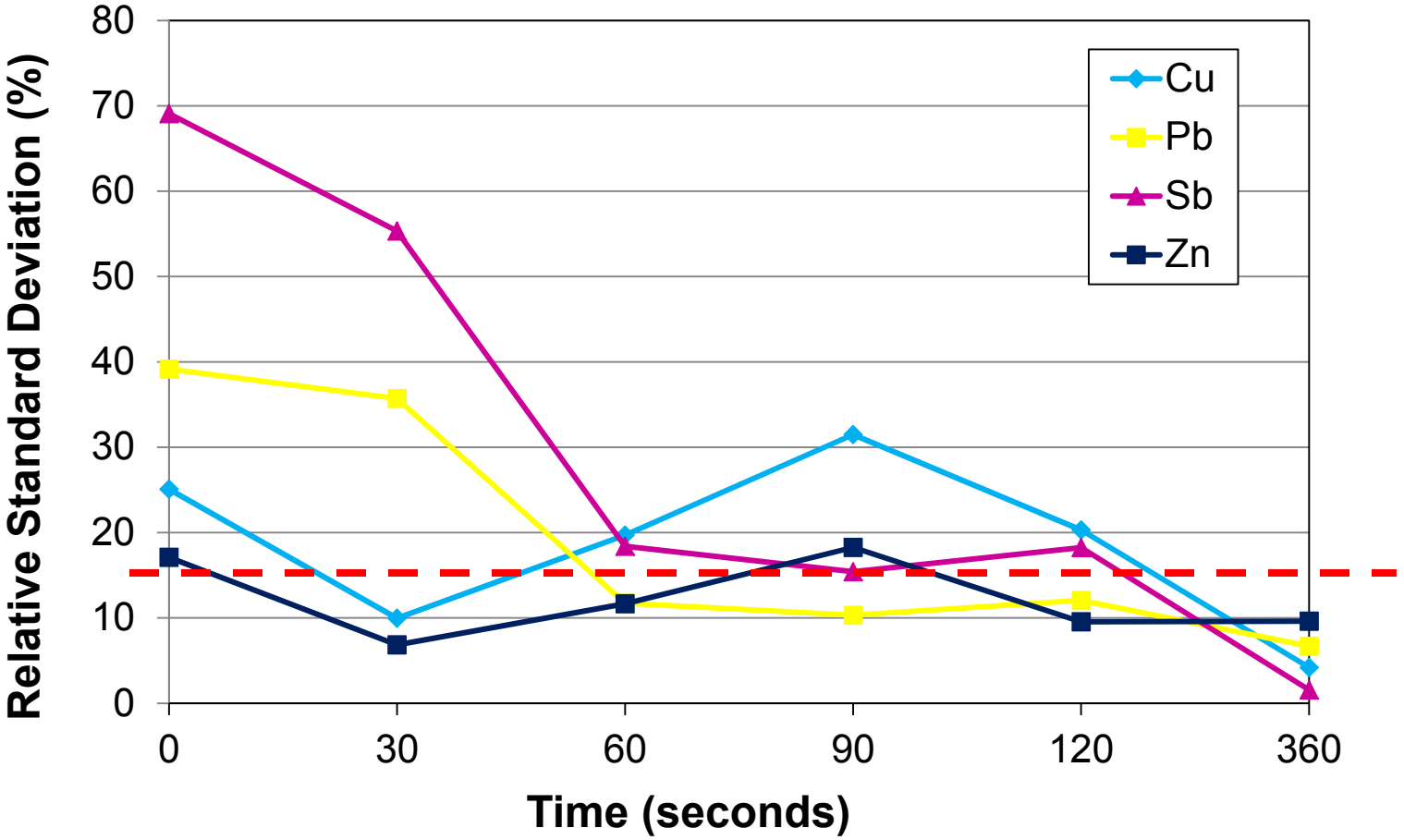
Alumina cans polyethylene
Liner, ceramic balls

Pulvisette

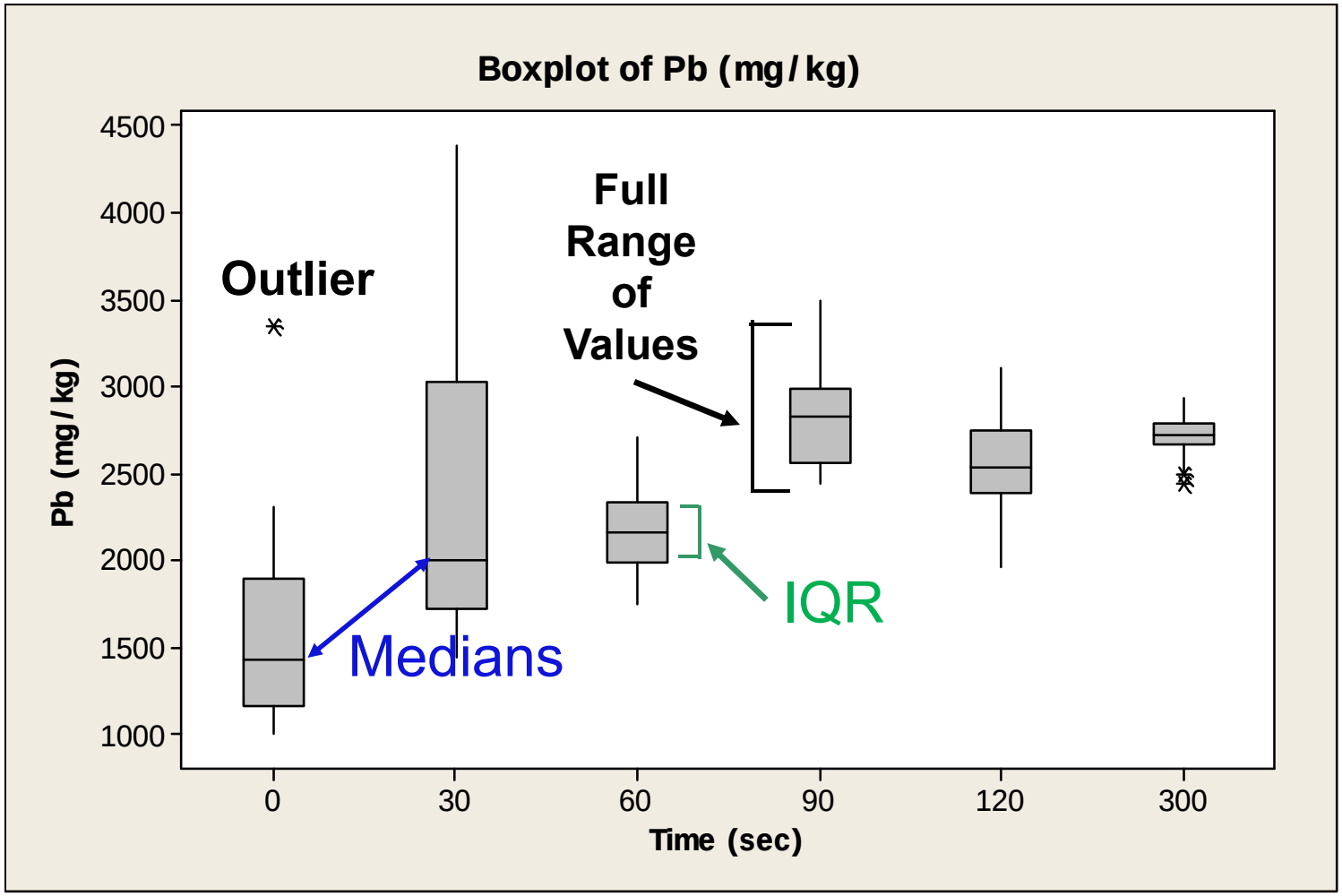
Agate balls

Mortar and Pestle
Ceramic

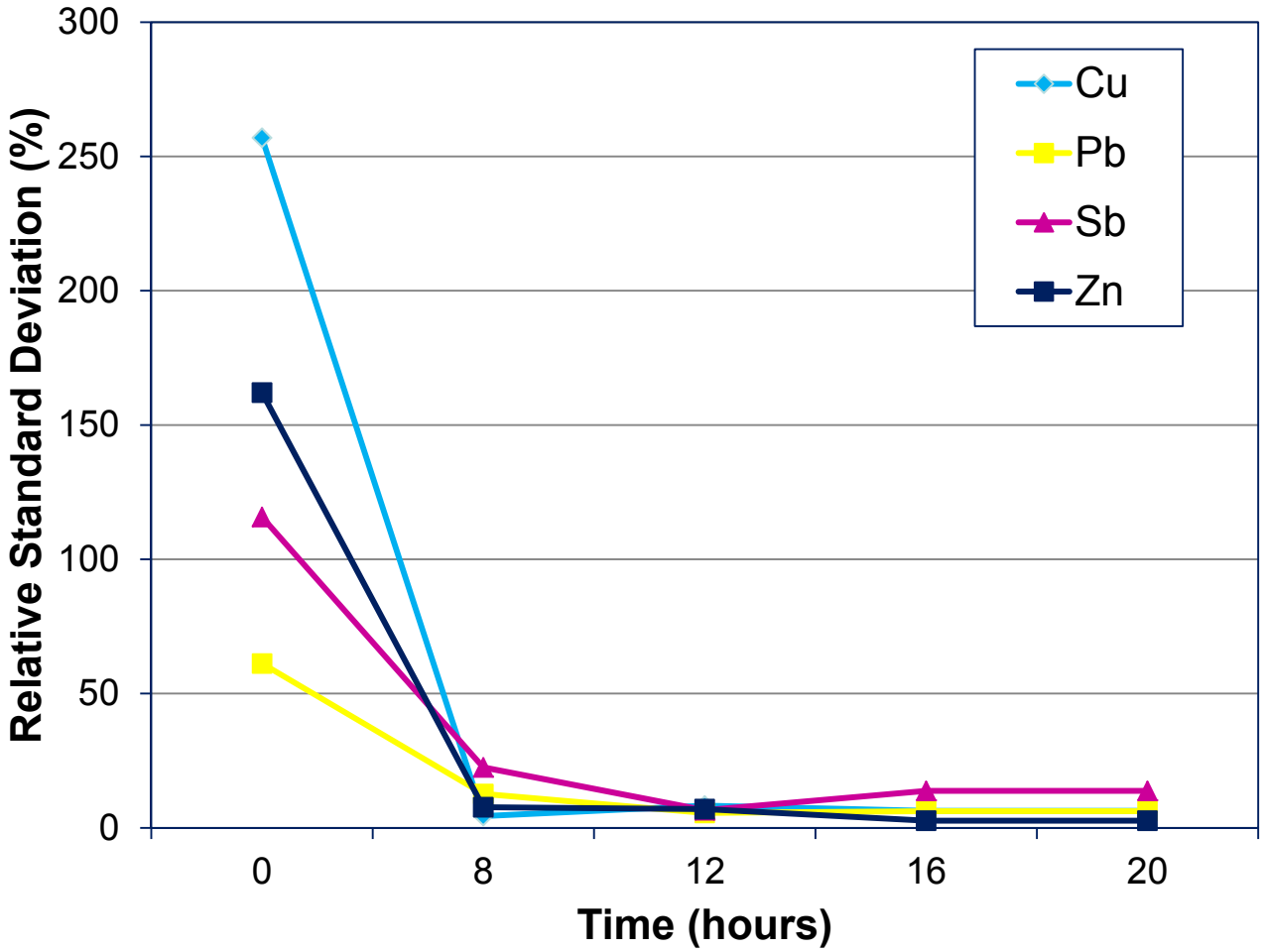
Puck Mill Optimum Grinding Interval



Puck Mill Optimum Grinding Interval



Roller Mill Optimum Grinding Interval



Milling Sample Contamination

	Cr	Cu	Fe	Mn	Ni	Pb	Sb	V	Zn
Mill Metal Conc. (mg/kg)	112,000	1,990	500,000	3,700	3,030	7	18.4	1,140	52
Mean Study Soil Conc. (mg/kg)	261	546	16,818	226	12	2,651	21	16	76
% Generic Contribution to Ground Sample (1 mg/kg)	99	4	14	24	47	<1	14	63	7
Contribution to Study Sample (%)	86	0.9	5.9	3.7	59	<1	4.9	20	1.4

Assumes 1 mg of material lost from puck mill and introduced to sample

Digestion Reagent Mixture

	Relative Standard Deviation (%)			
	Lead	**Lead Mod**	**Antimony**	**Antimony Mod**
Puck & Ring	37	5	39	9
Ball Mill - 8 hr	13	10	23	20
Ball Mill - 12 hr	6	4	7	7
Ball Mill - 16 hr	6	1	14	7
Ball Mill - 20 hr	1	1	1	2

Issues

- Considerable mass of metal remains in over size fraction (typically discarded)
- Ongoing question of impact of sample preparation method changes to risk determination
  - ♦ Does milling change the reported metal soil concentration
  - ♦ Is milling appropriate for assessing bioavailability
  - ♦ Does milling result in cross-contamination of the sample
- Poor recovery of antimony is evident with conventional analysis; new digestion process proposed

Conclusions

Activity	Yes	No
ISM, 30+ increments	√	
Discrete/Grab Sampling		√
Field Splitting		√
Sieving	√	
Milling necessity	√	
Increased digestion mass		√
Increased digestion time		√
Subsampling	√	